

HOMOGENOUS AQUEOUS ENERGY CURABLE METALLIC PRINTING INK COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

15

This application is a Continuation-In-Part of Application Serial No. PCT/US03/14293 filed May 6, 2003, now pending.

FIELD OF THE INVENTION

This invention relates to water based, energy curable printing ink compositions containing metallic colorants.

10

BACKGROUND OF THE INVENTION

Description of Related Art

15

Energy curable coating and ink compositions are typically composed of mixtures of acrylated derivatives such as oligomeric acrylates and monomeric acrylates. In most instances, the monomeric materials are employed in the composition to control the viscosity of the coating or ink formulation depending on the particular method of application. However, these monomers often do not react completely during polymerization upon energy curing. Unreacted monomers remain as residual components in the dried printing ink or coated film and are subject to migration by absorption as well as surface contact. This migration of residual components can lead to a host of problems such as "odor" and "off-taste" in sensitive packaging applications such as food packaging. Alternatively, solvents are used to reduce or manipulate the formulation viscosity for appropriate applications. However, the use of solvents is often associated with unacceptable emissions, toxicity, and/or odor levels for more sensitive product applications.

20

25

30

The undesirable characteristics of residual solvents and monomers in specialized coatings and inks has spurred advancement of water based, energy curable compositions, aqueous based curing, and the development of energy curable processes in the presence of water. While typically a poor solvent for organic compounds and

5 having too high surface tension to wet many polymer substrates, water in this instance may nevertheless be the ideal solvent for coating and ink delivery, able to lower viscosity and volatilize without adding to emissions, toxicity, or odor. The challenge is to formulate water compatibility over a wide range of compositions without producing water sensitivity and low rub resistance after curing.

10 An example of an energy curable composition can be found in EP 287,019. This reference, describes a composition wherein the oligomer is a carboxylic acid containing reaction product of a styrene maleic anhydride copolymer and a hydroxy(meth)acrylate. The composition further contains an ethylenically-unsaturated reactive diluent, a photoinitiator, and optionally a thiol. Exposure of the composition to an actinic source,
15 e.g. a UV light source, results in an aqueous-developable material useful in making printing plates and photoresists. Such a composition would be less useful as a protective coating or a binder in ink specifically due to the designed sensitivity to aqueous development, which would lead to low rub resistance when contacted by water.

20 Another example of an aqueous developable, energy curable composition can be found in EP 287,020. This reference describes an oligomeric material as the reaction product of a mono(meth)acrylate derivative of a caprolactone diol and styrene-maleic anhydride copolymer. The composition further optionally contains a reactive diluent and a photoinitiator. Exposure of the composition to a source of actinic radiation results in a
25 solid cured product useful for making printing plates and photoresists wherein the exposed compositions are developed using an alkaline aqueous developer. Again, such a composition would be less useful as a protective coating or ink binder due to its water sensitivity.

In neither of the above cases is delivery of the composition by aqueous solution
30 actually described. U.S. Patent No. 5,665,840 discloses a water soluble, crosslinkable prepolymer having in its copolymer chain, as monomeric structural units, a vinyl lactam; a vinyl alcohol; optionally a lower alkane number carboxylic acid vinyl ester; a vinyl crosslinking agent; and optionally a vinylic photoinitiator. This reference also discloses a process for making prepolymers, as well as crosslinked, water insoluble, polymeric
35 networks particularly useful for making hydrogels and water absorbing, molded articles such as contact lenses. Because these cross-linked, water insoluble, polymeric networks swell with water, they would be unsuitable as cured protective coatings and ink vehicles where they would exhibit low resistance to mechanical abrasion when in the presence of moisture.

5 U.S. Patent No. 4,745,138 discloses a class of low molecular weight, partial esters of anhydride containing copolymers capable of providing non-aqueous, energy curable, liquid compositions for production of radiation-hardenable coatings without the need to employ an inert organic solvent. These compositions employ monomers containing terminally ethylenically unsaturated groups and maleic anhydride copolymers
10 characterized by having free anhydride functionalities and are said to be particularly suitable for improving adhesion and the dispersive capabilities of binder resins. The partial esters are produced by esterifying a fraction of the anhydride groups by ring-opening with a hydroxyalkyl acrylic compound or an admixture thereof with a monohydric alkyl alcohol. By virtue of the introduction of hydrophobic substituents
15 (particularly the esters of monohydric alkyl alcohols) and the absence of carboxylic acid groups, these compositions cure to films, which are more water- and solvent-resistant than those made in accordance with the previous references. However, not discussed in this patent are aqueous solutions of these polymers as provided by hydrolysis of the residual anhydride in dilute caustic, the use of these solutions to stabilize solutions or
20 colloidal dispersions of other, less polar materials, or coating or ink compositions prepared with these solutions.

A parallel approach uses solutions of acrylated, hydrophilic oligomers alone or together with the fore-mentioned polymers. Acrylated oligomers (and solutions of polymer resins made with oligomers) have a viscosity that is typically too high to be
25 used directly for making coatings and printing inks. The use of water as a diluent to lower the viscosity of energy curable, acrylated, oligomeric mixtures has been described in U.S. Patent 6,011,078 wherein the mixtures are used for wood and floor coating applications. The formulations taught in this patent are dispersions or emulsions and require prior evaporation of water followed by exposure to a temperature above the
30 minimum film formation temperature (MFFT) before exposure to the actinic source. Without film formation prior to cure, the resultant energy cured, crosslinked polymer has very weak coherence, lacks adherence to a substrate, and does not provide the rub resistance required. Further, the additional drying step(s) slow the press speed and increase the potential for causing surface defects (e.g., lower gloss).

35 Acrylic functional polyesters containing salt structures are described by M. Philips, J.M. Loutz, S. Peeters, L. Lindekens, *Polymers Paint Colour J.*, 183, #4322, p.38 (1993). These are combined with hydrophilic monomers (e.g., polyethyleneglycol diacrylates) and water to make radiation curable, protective coatings. The combinations are described as homogeneous solutions that can be coated and radiation cured by UV

5 with water-soluble photoinitiators to give rub- and wash-resistant top-coats. Also, see J. M. Loutz, S. Peeters, L. Lindekens, J. Coated Fabrics, 22, p.298 (1993). In reality, all these formulations are very limited in the amount of water that can be incorporated and are comprised of high resin mass fraction (greater than 65 wt. % of vehicle) with consequently high viscosity. Typically, greater than 30 wt. % water on a total liquids
10 (vehicle) basis causes degraded performance in the examples provided. Due to this fact, less than 10 wt. % water is recommended; and even at this water content, "a thermal flash-off step is recommended in order to avoid the formation of microporosity in the film."

To make water based printing inks that: do not require drying prior to cure, cure
15 to well-adhered, offer rub-resistant films, and are characterized as low-odor and low-extractable, mixtures of highly-functional, acrylated oligomers and polymers in aqueous solution or in a thermodynamically stable aqueous microemulsion at viscosities below 500 cP (25 deg C, 10 s-1) as tolerated on typical presses (e.g., flexo, gravure, and rotary screen) are needed. The formulation of such systems to contain both hydrophilic
20 and hydrophobic components, highly functional polymers and oligomers, and at water levels exceeding 25 wt. % (not including dispersed solids) to provide control of viscosity without sacrifice of cure speed is a challenge not met in the prior art.

SUMMARY OF THE INVENTION

25

The invention is an energy curable, aqueous, printing ink composition comprising a metallic colorant in a homogeneous vehicle having as its components water, an ethylenically unsaturated oligomer, and an ethylenically unsaturated resin containing neutralized acidic or basic functional groups. Preferably, these components are in such
30 proportions and structures as to achieve greater than 25 wt. % water at less than 60 wt. % resin in the vehicle portion.

A further embodiment of the invention is an energy curable, aqueous printing ink composition comprising a metallic colorant in a homogenous vehicle having as its components water and an ethylenically unsaturated resin containing neutralized acidic
35 or basic functional groups. Preferably, these components are in such proportions as to achieve greater than 40 wt. % water in the vehicle.

The conditions under which the described compositions are defined as homogenous are given by the temperature, humidity and pressure in the environment prevailing at the moment of cure. In addition, it is preferred that the liquid vehicles of

5 the compositions also be at ambient temperature, humidity, and pressure.

A further embodiment of the invention is a method for printing using an energy cured, water resistant metallic printing ink on a substrate comprising: applying to a substrate an energy curable, aqueous homogeneous composition, as described herein combined with a metallic colorant, then subjecting the printed substrate to an actinic radiation source prior to removal of the water thereby forming an energy cured, water resistant metallic print.

Other objects and advantages of the present invention will become apparent from the following description and appended claims.

15 BRIEF DESCRIPTION OF THE DRAWINGS

The invention can be more fully understood by use of the accompanying drawings.

Figure 1 is a three-component, triangular, phase diagram in which the components are: (A) water; (B) a partially water soluble oligomer; and (C) a water-soluble, ethylenically unsaturated resin. Each vertex is a pure component and each point on and within the diagram corresponds to a mass fraction (or expressed as wt. %) of each of the three possible components such that the sum of mass fractions is 1.0 (or 100 wt. %). Each mass fraction is read by construction of three lines parallel to the side opposite the vertex for the pure component in question and reading off the intersection of these lines (e.g., a-a', b-b', c-c' for point (18)) on the binary blend scales which are the sides of the figure. We are interested in the low viscosity, homogenous or regions in this diagram.

Figure 2 is a four-component, tetrahedral, phase diagram in which the components are: (A) water; (B) a partially water soluble oligomer; (C) a water soluble, ethylenically unsaturated resin; and (D) a water insoluble oligomer. Again, each vertex is a pure component and each point on or within the diagram corresponds to a mass fraction (or expressed as wt. %) of each of four components such that the sum of mass fractions is 1.0 (or 100 wt. %). The mass fractions are read by the intersection of planes parallel to face opposite the vertex for the pure component in question with the binary blend scales that are the sides of the figure. **Figure 1** is one face of this tetrahedron (where the mass fraction of component D is zero). We are interested in the low viscosity, regions that contain D in this diagram.

5

DETAILED DESCRIPTION OF THE INVENTION

The present invention teaches the preferred use of homogenous, aqueous, energy curable compositions in the manufacture of printing inks. These compositions may be formed as ternary or quaternary solutions or as microemulsions comprised of
10 (A) water; (B) water soluble oligomers; (C) water soluble, ethylenically unsaturated resin; and optionally, (D) a water insoluble oligomers. These components are preferably in such proportions and structures as to achieve greater than 25 % wt. % water in the total liquid (vehicle) portion with less than 60 wt. % of the solubilizing resin. In the homogenous solutions of the present invention, the resin contains neutralized
15 acidic or basic functional groups which renders it soluble in the final aqueous composition. Further, in the present invention the proportion of water may be freely adjusted so as to achieve any target application viscosity and assure complete cure in processes where drying and curing occur simultaneously without inerting.

In the present invention, as in the prior art, water is used largely as a diluent to
20 control the viscosity of the composition. But in contrast to prior art coating formulations, the invention demonstrates a way to extend the compatibility of water in the composition to a much higher level than previously achieved. With an increase in water compatibility, we are able to use water to create low odor formulations since we can now use higher molecular weight (meth)acrylated components while still maintaining an
25 appropriately low viscosity. The resin is completely soluble in water when even partially neutralized, and it is so structured so as to allow for a mixture (i.e. solutions) of ingredients by functioning as a "solubilizing" aid. To accomplish this, the resin comprises both hydrophobic and hydrophilic segments. Only the water insoluble oligomer of the major components listed does not contribute to stabilize an aqueous,
30 composition. Instead, its level is allowed for by the incorporation of hydrophobic elements into the resin and the partially water soluble oligomer.

As used herein the term "solution" is intended to have the conventional meaning as a homogeneous mixture formed by dissolving one or more substances into another substance, i.e. a liquid or solid. As used herein the term "miscible" is intended to mean
35 that two or more components form a solution. As used herein the term "water soluble" is intended to mean that a component is miscible in water over an extensive concentration range, e.g. > 0 – 90 wt. % water or more in the total mass of the liquid (vehicle) portion, to form a homogenous aqueous solution. As used herein the term "partially water soluble" is intended to mean that a component is miscible in water only

5 over a limited concentration range, e.g. >0 to 70 wt. % water, in forming a homogenous aqueous solution.

As used herein the term "microemulsion" is used to describe a clear, homogeneous, thermodynamically-stable, colloidal suspension of such small particle size that all the attributes of a true solution apply (except perhaps for the wavelength of
10 maximally scattered light). From this point, the term solution will imply that the described result may also be achieved by a thermodynamically stable microemulsion. This description is not to be confused with a metastable emulsion (as, for example, in an emulsion polymer), a coarser dispersion which is not truly thermodynamically stable but only kinetically stable. This does not imply that such kinetically stable emulsions are
15 not useful in admixture with the inventive solution, but that the base of the formulation is a solution of the components discussed within which a fourth or fifth emulsified component may be dispersed.

The term "energy curable", as used herein, is intended to mean a free radical, addition-cured, hardened, polymerizable, or crosslinkable composition, material, or
20 system or any addition-cured, hardened, or crosslinkable composition, material, or system, wherein the curing, hardening, polymerizing, or crosslinking occurs by action of an actinic radiation source such as ultraviolet light (UV), electron beam radiation (EB), and the like. As used herein "actinic radiation" is defined in its broadest sense as any radiation that is capable of exposing photographic film.

25 Free radical photoinitiating systems can be incorporated within the addition-cured systems of the solutions of the present invention in order to enhance the curing. Colorants can be incorporated using the solutions of the invention as a vehicle to produce water-based inks having excellent rheology and suitable for a wide range of printing applications from ink jet to higher viscosity paste ink applications. The
30 temperatures at which coating compositions are typically stored and used are about room temperature. Accordingly, those solutions stable at ambient temperature are desirable and achieved within the scope of the present invention. In addition, we require that the composition also be at the temperature pertaining at the point of cure.

The energy curable compositions of the present invention may be more fully
35 understood from the following description provided in connection with **Figures 1 and 2** of the accompanying drawings. Throughout the description herein, similar reference characters refer to similar elements in all figures. The term component includes single molecular species (pure components) and mixtures of similar components termed pseudocomponents that partition between phases in the multiple phase regions of the

5 phase diagram without alteration of the relative abundance of each component of the pseudocomponent in each phase. Also as used herein, the term "major component" is intended to mean a component (or pseudocomponent) having greater than 5 wt. % concentration in the compositions of the present invention. The figures contained in the drawings are intended only as illustrations of the ternary and quaternary, aqueous,
10 energy-curable compositions of the present invention and are not necessarily drawn to scale or to reflect any actual phase transition boundary between phase regions in the phase diagram.

The region of most interest in the triangular phase diagram (10) in **Figure 1** is enclosed by the cross-hatched trapezoidal fragment (15) with its high resin content limited by the 60 wt. % resin line; its low resin content defined by the cloud point curve
15 (12); its low water side by the 25 wt. % water line; and its high water side by the resin / water binary (line (A-C)). Over this region, the composition is homogenous and inventive. The viscosity can be varied by varying the water and/or resin mass fractions to match that required by the press speed and the application technique. Curing is
20 rapid by virtue of the lower oxygen solubility in this region.

The phase transition boundary (12), i.e. the cloud point curve, defines the component concentrations at which the ternary mixture transitions from two phases in region (14) to the sum of regions (15) and (16). It is understood that the phase transition boundary (12) may assume any shape. Further, its placement within the
25 phase diagram (represented by the arrows "<----->" about points x, y, and z), depends on the specific partially water-soluble oligomer and specific resin chosen in the ternary mixture as well as other factors such as the exact temperature at the point of cure, the pressure in the nip, and interaction with other non-major components of the composition such as wetting agents and photoinitiators.

30 The solubility in water of the partially water-soluble oligomer and the water-soluble resin is further illustrated by the binary mixture portion of the diagram represented by base (A_B) and base (A_C), respectively. The water / partially water-soluble oligomer mixture concentrations are defined by points along base (A_B) which contains the cloud point X where a homogenous solution converts to a two-phase
35 mixture. Thus, mixtures falling within the base segment (A_X) are two-phase mixtures, while the mixtures falling within the base segment (X_B) are homogenous solutions in this illustration. Accordingly, the oligomer may be termed "partially water soluble" for the purposes of this invention when the quantity represented by the line segment (A_X) is greater than 30 % of the total segment (A_B).

5 The water / water-soluble solubilizing resin mixture concentrations are defined by points along base (A_C) which contains the cloud point Y where a homogeneous solution converts to a two phase mixture. Thus, mixtures falling within the base segment (A_Y) are two phases, while mixtures falling within the base segment (Y_C) are homogenous solutions. Accordingly, the resin may be termed "water soluble" when
10 the quantity represented by the line segment (Y_C) is greater than 30 % of the total line segment (A_C).

 In **Figure 2**, an additional component D, the water insoluble oligomer, has been added. **Figure 1** is reproduced in **Figure 2** as the forward-most triangular face of the tetrahedral phase diagram (20) where the mass fraction of D is zero. The cloud point
15 curve (12) is also illustrated in this face. Another important phase boundary (22) is shown on the A-B-D face which shares one point on the A-B binary with the previously discussed cloud point curve and extends to point D. Referring to the internal box-like volume segments (19) and (23) of the tetrahedral phase diagram, the phase-transition boundary surface segments b-b'-b"-b'" (28) and a-a'-a"-a'" (25) represent regions of an
20 internal cloud point surface which defines the component concentrations at which the phase-transition for the quaternary mixture occurs from two phases in concentration region (24) to concentration region (26) summed over the entire diagram. It is understood that the phase-transition boundary may assume any shape. Further, its placement within the phase diagram depends on the specific partially water-soluble
25 oligomer, resin, and water-insoluble oligomer employed in the quaternary mixture as well as other factors such as the exact temperature and the interaction with other non-major components of the composition.

Water

30 A major component of the compositions of the present invention is water. Water functions as an odor-free diluent used to adjust the viscosity of the composition. Further, water in such quantities as to be retained whole or in part in the applied liquid at the point of cure provides the polymer segment mobility needed for a high degree of
35 cure. And finally, the decreased solubility of oxygen in aqueous media contributes to a rapid rate of cure in the absence of inerting. All these benefits are increased as the proportion of water in the formula is increased. The viscosity's of these solutions can all be adjusted by adjusting the proportions of the miscible diluent and the remaining oligomer provided that the resulting liquid remains a homogenous liquid, preferably with

- 5 water fractions greater than 25 wt. % in the homogenous liquid. The latter is an important point not only for the freedom to adjust viscosity but also in order that water above a certain limit be provided at the point of cure to maintain fluidity and low oxygen tension when curing and drying are occurring simultaneously.

10 **Water Soluble Ethylenically Unsaturated Oligomer**

The water soluble oligomer (or the partially water soluble oligomer, vide infra) functions as a lower molecular weight extender. It is typically multifunctional, comprising at least two (meth)acrylate groups. The major requirement other than
15 solubility is that it rapidly builds into the network after initiation of polymerization. The wt. ratio of resin to water-soluble oligomer extender generally ranges from 2.0 to 0.2, preferably 1.0 to 0.4, and most preferably 0.7 to 0.6. The exact choice depends on the structure of both the resin and the oligomeric extender and the type of property most desired (e.g., scratch resistance or water resistance).

20 The water soluble oligomer preferably forms an aqueous solution within restricted proportions of the oligomer/water components. Thus, a "partially water soluble oligomer" is an oligomer that is miscible in water but only over a limited concentration range, e.g. > 0 - 70 wt. % water in the total mass, to form a homogenous aqueous solution. As defined earlier in reference to base segment (A_B) in the accompanying
25 figures, an oligomer is "partially water soluble", as defined by the phase diagram, when the quantity of oligomer represented by the line segment (A_X) is greater than 30 % of the base segment (A_B). Typically, line segment (A_X) ranges between 30 % to about 90 % of the total base segment (A_B).

The water soluble oligomer is further characterized as a monomer or macromer
30 containing ethylenic unsaturation and which can be polymerized or cross-linked by free radical polymerization. It also contains sufficient water-solubilizing groups such as hydroxyl groups, ethylene oxide segments, and the like to assure at least 5 % water uptake in the oligomer / water binary. Preferably, the water soluble oligomer is, for example, selected from acrylates, methacrylates or combinations thereof. Typically, the
35 water soluble oligomer will contain one or more acrylate or methacrylate groups. Acrylates or methacrylates useful as water soluble oligomers in the present invention may, for example, be selected from the group consisting of epoxy acrylates, epoxy methacrylates, polyether acrylates, polyether methacrylates, polyester acrylates, polyester methacrylates, polyurethane acrylates, polyurethane methacrylates, melamine

5 acrylates, melamine methacrylates, ethoxylated trimethanolpropane acrylate, ethoxylated trimethanolpropane methacrylate, ethoxylated di(trimethanolpropane) acrylate, ethoxylated di(trimethanolpropane) methacrylate, ethoxylated pentaerythritol acrylate, ethoxylated pentaerythritol methacrylate, ethoxylated dipentaerythritol acrylate, ethoxylated dipentaerythritol methacrylate, ethoxylated neopentaglycol acrylate,
10 ethoxylated neopentaglycol methacrylate, ethoxylated propylene glycol acrylates, ethoxylated propylene glycol methacrylates, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates. Particularly preferred oligomers are alkyl epoxy acrylates and alkyl epoxy methacrylates.

The water soluble oligomer component may be a single oligomer or a
15 combination of two or more oligomers as described above. In the case, a combination is used, a single pseudocomponent (B') is substituted for the pure component (B) in the phase diagram without any additional condition. The employment of pseudo-components to simplify phase diagrams is well known in the art.

Typically, where the oligomer is a partially water soluble oligomer, it accepts at
20 least 5 % water to form an aqueous solution, and preferably accepts 10 % or more water.

In addition, the water soluble oligomer may be too compatible with water (line (A_X) less than 30 % of line (A_B) in Figure 1). When the water soluble oligomer (or the blend of water-soluble oligomers) is present in greater than 50 wt. % of the total
25 solids obtained by evaporation of the water from the total liquid (vehicle), the water-soluble oligomer (or the blend) should accept no more than 70 wt. % water in a binary (or pseudo-binary) oligomer-water, liquid solution. The result of too high water compatibility is that the water resistance of the final cured film will be degraded.

30 Water Soluble, Ethylenically Unsaturated Resin

The water soluble, ethylenically unsaturated resin forms a stable, homogenous composition with extensive proportions of the oligomer / water binary components, comprising at least 10 to 80 wt. % or more water in the total liquid. As defined earlier in
35 reference to the line segment (A_C) in the accompanying figures, a resin is "water soluble" if, as defined by the phase diagram, the quantity represented by the line segment (C_Y) is greater than 30 % of segment (A_C). Typically, line segment (C_Y) ranges between 60 % to 95 % of the total base segment (A_C), although the water soluble resin may form solutions throughout the concentration range represented by the

5 total segment (A_C).

The word resin has its usual connotation for ink and coatings, i.e., a hard solid polymer showing properties typical of higher molecular weight provided by hydrogen-bonded structures without actually being high molecular weight. The preferred weight average molecular weight is greater than 1000 but less than 100,000 daltons, more
10 preferably greater than 1000 but less than 50,000 daltons, and most preferably greater than 1000 but less than 10,000 daltons.

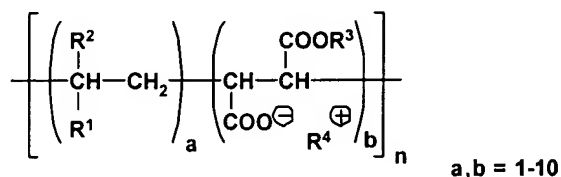
Further, in the present invention, the water soluble resin is a particular type of surface-active material that functions as a "solubilizing" agent, capable of assisting in the dissolution of other water-insoluble components into aqueous solution. It does this
15 by chemically incorporating substantial hydrophilic (e.g., ionic and hydrogen-bonding groups such as carboxyl) and hydrophobic (e.g., hydrocarbon) structures (as pendant groups or as main chain segments). For example, the resin may have acid-functional groups (e.g. pendant carboxylic acid groups) which are partially or totally neutralized with a base (e.g., an amine) to form a water-soluble resin salt. Alternatively, the
20 polymeric resin may have basic functional groups (e.g. amino groups) which are partially or totally neutralized with an acid (e.g. a carboxylic acid) to form a water soluble resin salt. Preferably, the resin contains at least two acrylic groups, methacrylic groups, or a combination thereof, per molecule; more preferably three to five per mole; and most preferably more than six such functions per mole. The carboxylic acid functional groups,
25 which are neutralized with a base, are in such number as to generate an acid number of greater than 80 (mg of KOH to completely neutralize 100 g of resin) to assure water solubility over at least a portion of the water/resin binary. And preferably, the resin also contains hydrophobic substituents (e.g., esters of aliphatic alcohols) to an extent that generates good pigment dispersing properties, water resistance, and properties
30 consistent with the above requirements. Thus a preferred ethylenically unsaturated resin is a neutralization product of a base with an energy curable polymer or resin containing carboxylic acid groups; acrylic groups and/or methacrylic groups; and esters of hydrophobic alcohols, wherein the neutralization product is a water soluble, acrylated, resin salt.

35 A particularly preferred energy curable resin is a styrene/maleic anhydride copolymer partially esterified with a hydroxy alkyl acrylate or methacrylate, (e.g., hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxybutyl acrylate, or hydroxybutyl methacrylate) and a medium chain-length aliphatic alcohol (e.g., n-propanol, n-butanol, amyl alcohol, isoamyl alcohol, and the like). By increasing the proportion of

5 hydroxybutyl (meth)acrylate to hydroxyethyl (meth)acrylate, the proportion of methacrylate to acrylate, the proportion of normal (unfunctional) alcohol to functional or branched alcohol, and the proportion of longer-chain alcohol to shorter-chain alcohol, the hydrophobicity of the resin can be increased. In addition, by decreasing the proportion of total esterification, increasing the extent of neutralization of the acid groups by caustic, or by the choice of more highly hydrated caustic (e.g., lithium hydroxide), the hydrophilicity can be increased. By use of these tools, the resin can be made to be water-soluble, to stabilize colloidal dispersions and solutions of water-insoluble oligomers, to stabilize pigment dispersions, and yet to resist water in the final cured product.

15 An example of an energy curable polymer of this type is disclosed in PCT International Patent Application WO 99/193669, which is incorporated herein by reference. Accordingly, a preferred resin salt is a resin concentrate containing 39 - 41 wt. % resin solids in water and neutralized with ammonia to a pH of 6.5. The resin is energy curable having the general structure:

20



$\text{R}^1, \text{R}^2 = \text{H}, \text{C}_1 - \text{C}_{18} \text{ Alkyl}, \text{Phenyl}, \text{Toluy}, \text{C}_7 - \text{C}_{14} \text{ Alkaryl}, \text{C}_4 - \text{C}_{12} \text{ Cycloalcyl}, \text{Cl}, \text{F}, \text{Br}$

$\text{R}^3 = \text{C}_1 - \text{C}_{18} \text{ Alkyl}, \text{C}_4 - \text{C}_{12} \text{ Cycloalcyl}, \text{C}_3 - \text{C}_{10} \text{ Polyester},$

$(\text{CR}^6\text{HCH}_2\text{O})_n\text{R}^7, (\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n\text{R}^7, \text{R}^5\text{OCOCHR}^6=\text{CH}_2$

$\text{R}^4 = \text{H}, \text{Ammonia}, \text{Amine}, \text{Alkalimetal}$

$\text{R}^5 = \text{C}_1 - \text{C}_{18} \text{ Alkyl}, (\text{CR}^6\text{HCH}_2\text{O})_n, (\text{CH}_2)_4\text{COOCH}_2\text{CH}_2, \text{C}_3 - \text{C}_{10} \text{ Polyester}, \text{CH(OR}^3\text{)CH}_2\text{OC}_6\text{H}_4\text{OCH}_2\text{C(OR}^3\text{)CH}$

$\text{R}^6, \text{R}^7 = \text{H}, \text{C}_1 - \text{C}_5 \text{ Alkyl}$

While any basic compound (e.g., alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, or lithium hydroxide or amines such as ammonia, alkyl amines, or amine-containing oligomers) may be used to neutralize the acidic groups of the resin, ammonia, amines or combinations thereof, are preferred. A preferred base is selected from tertiary amines. In a particularly preferred embodiment, the base is an ethylenically unsaturated tertiary amine as described in co-pending U.S. Patent

5 Application USSN_____. With selected, alcohol functional, ethylenically unsaturated, tertiary polyamines as neutralizing agents, the acid groups on the resin may be totally neutralized to form a cross-linkable, water soluble ionomer. The ethylenically unsaturated tertiary amine provides the counter ion of the acidic resin and allows the ionomer formed to "stereo" polymerize during photoreaction to form an additional cross-linked network over the ethylenically unsaturated groups as well as over the ionic structure. Unlike other water based, energy curable, resin technologies (wherein the water resistance is imparted to the resin film by the evaporation of ammonia, for example, which shifts the acid base equilibrium in the post-cured material), here by using an ethylenically unsaturated base, the neutralized resin forms an additional cross-linked network instantly on both sides of the ionomer by radiation induced free radical addition polymerization. The result is an energy cured film having enhanced solvent and water resistance from the interpenetrating network of covalent and ionic bonds and improved gloss from more rapid surface cure.

20 Water Insoluble Ethylenically Unsaturated Oligomers

The water insoluble oligomers suitable for use in the present invention are energy curable and form two phase mixtures with water within extensive proportions of the water insoluble oligomer / water binary composition space (line segment (A-D) in **Figure 2**). As defined earlier in reference to the line segment (A_D) in the accompanying **Figure 2**, the water insoluble oligomer is typically insoluble over the total water / oligomer concentration range represented by the segment (A_D). However, an oligomer which is capable of incorporating 5 wt. % water or less is also included as water insoluble for the purpose of this invention.

30 While the water insoluble oligomer typically is totally immiscible in water, the water insoluble oligomer may form a solution with the water soluble oligomers within extensive proportions of the (water insoluble oligomer) / (water soluble oligomer) binary compositions. The water insoluble oligomer is preferably miscible in the water soluble oligomer over an extensive concentration range, e.g., 5 to 95 wt. % water insoluble in the total blend, to form a binary solution. Typically, the water insoluble oligomers are compounds (or mixtures of similar compounds), which have one, two, or more terminal ethylenically unsaturated groups. Representative of such compounds, for example, include: dipropylene glycol diacrylate; tripropylene glycol diacrylate; butanediol diacrylate; hexanediol diacrylate; alkoxyated hexanediol diacrylate; trimethylol propane

5 triacrylate; alkoxyated trimethylol propane triacrylate; di(trimethylol propane triacrylate); glycerolpropoxy triacrylate; pentaerythritol triacrylate; alkoxyated pentaerythritol triacrylate; di(pentaerythritol triacrylate); neopentaglycol diacrylate; alkoxyated neopentaglycol diacrylate; dipropylene glycol dimethacrylate; tripropylene glycol dimethacrylate; butanediol dimethacrylate; hexanediol dimethacrylate; alkoxyated
10 hexanediol dimethacrylate; trimethylol propane trimethacrylate; alkoxyated trimethylol propane triamethacrylate; di(trimethylol propane methtriacrylate); glycerolpropoxy trimethacrylate; pentaerythritol trimethacrylate; alkoxyated pentaerythritol trimethacrylate; di(pentaerythritol trimethacrylate); neopentaglycol dimethacrylate; alkoxyated neopentaglycoldimethacrylate; and the like and combinations thereof. The
15 water-insoluble oligomer may contain a combination of diacrylic and triacrylic monomers along with a monomer containing a single terminal ethylenic group. The water insoluble oligomers may be acrylated epoxy resins; bis acrylic esters of bisphenol A; acrylated polyurethanes; acrylated polyesters; acrylated polyether and the like. Preferred water-insoluble oligomers of this type include di-(3-methacryloxy-2-hydroxypropyl ether of
20 bisphenol-A; di(2-methacryloxyethyl ether of bisphenol-A; di-(3-acryloxy-2-hydroxypropyl ether of bisphenol-A; di(2-acryloxyethyl ether of bisphenol-A; and the like.

Binary Aqueous Homogeneous Solutions Containing Resins

25 A binary, aqueous embodiment of this invention is an energy curable, aqueous composition comprising a solution of water and a water soluble, ethylenically unsaturated resin salt wherein the resin salt is comprised of, for example, the neutralization product of ammonia, an amine or an ethylenically unsaturated tertiary amine and an ethylenically unsaturated resin containing acidic-functional groups. As
30 discussed previously in connection the water soluble, ethylenically unsaturated resin salt, the ethylenically unsaturated resin contains acrylic groups, methacrylic groups or a combination thereof and is neutralized by ammonia, an amine or an ethylenically unsaturated tertiary amine to form the resin salt. The nature of the water soluble, ethylenically unsaturated resin salt and the water soluble oligomer has been discussed
35 above, and those discussions apply to this embodiment of the invention.

5 **Ternary Aqueous Homogeneous Solutions Containing Water Soluble Oligomers and Resins**

Figure 1 illustrates the ternary, energy curable compositions of this invention. This embodiment is an energy curable, aqueous composition comprising a solution of
10 water; a free radical addition-polymerizable, water soluble oligomer or alternatively a partially water soluble oligomer; and a water soluble, ethylenically unsaturated resin salt. The general nature of this embodiment was discussed above. Likewise, the natures of the water soluble, ethylenically unsaturated resin salt and the water soluble oligomer have been discussed above. These discussions apply to this embodiment of
15 the invention.

 The limit of water solubility of the oligomer is expressed by the position of Point X in **Figure 1**. In this invention, it is preferred that X comprise more than 10 wt. % and less than 70 wt. % water and most preferred that X comprise more than 20 wt. % and less than 40 wt. % water. If point X comprises less than 10 wt. % water (is too close to
20 point B), the two-phase region ((14) in **Figure 1**) will be too large, extending so far towards point C at point Z that the resulting solutions above point Z become too viscous for use in common graphic arts applications. Similarly, if point X comprises more than 70 % water, the resulting cured polymer will be too water-sensitive to be useful as a protective coating.

25 The preferred ternary compositions comprise stable, compositions within region (15) in phase diagram (10) of **Figure 1**. The properties of the preferred compositions within this region can be adjusted by the choices of oligomer A and resin C as will be apparent from the Examples, below.

30 **Quaternary Aqueous Homogeneous Solutions Containing Water Insoluble Oligomers Water Soluble Oligomers and Resins**

Figure 2 illustrates the quaternary, energy curable solutions of this invention. This embodiment is an energy curable, aqueous composition comprising a composition
35 of water; a free radical addition-polymerizable, water soluble oligomer or, alternatively, a partially water soluble oligomer; a free radical addition-polymerizable, water insoluble oligomer, and a water soluble, ethylenically unsaturated resin salt. The general nature of this embodiment was discussed above. Likewise, the nature of the water soluble, ethylenically unsaturated resin salt, the water soluble oligomer and the water insoluble

5 oligomer has been discussed above, and those discussions apply to this embodiment of the invention.

The region of most interest in **Figure 2** is a volume of limited extension toward the water insoluble component (D) which originates in the region of face ABC (identical to **Figure 1**) near the cloud point curve (12). Its general shape in the (D) direction is indicated by the cloud point curve (22) in the ABD face that quickly limits the water content to below 25 wt. % of the total liquid in the region to the left of the A'B'C' plane (toward higher (D)). Thus the present invention is limited to the region bound between plane A'B'C' on the left and the ABC plane on the right, by the 25 wt. % water plane on the bottom and the complex surface which is the cloud point surface which approximately follows the planes (a,a',a'',a''') and (b,b',b'',b''') summed over the entire tetrahedral space. Alternatively, the extent of the quaternary, region is controlled by the total amount of hydrophobic material component (D) including that portion coming from the partially water soluble component (B) and any coating or curing additive (vide infra) which a given structure and amount of the resin (C) can compatibilize with substantial water.

The addition of (D) to water-rich point (23) transitions from a homogeneous solution to a composition which is more likely to be an oil-in-water microemulsion (o/w) near the plane (a,a',a'',a''') in which the continuous phase is aqueous with microscopically small dispersed domains of (D), smaller in diameter than the wavelength of visible light. Similarly, the addition of (D) to oil-rich point b' near the AB axis transitions from a solution to a composition which is more likely to be a water-in-oil microemulsion (w/o) near the plane (b,b',b'',b''') in which the continuous phase is largely oligomer B with microscopically small dispersed domains of (D) dispersed within.

By adjusting the balance between the number and nature of the hydrophobic ester groups (to compatibilize the resin with the water-insoluble oligomer) and the extent and nature of the neutralization of the acid groups (to compatibilize the resin with the water and water-soluble oligomer), the volume within **Figure 2** can be increased. When successful, there exist homogeneous, quaternary compositions at such proportions that they contain greater than 25 wt. % water and greater than 5 wt. % (D) that are particularly useful in the direct cure of inks based on these compositions as vehicle without prior drying.

5 Free Radical Photoinitiator

Any of the previously described energy curable, homogeneous, aqueous compositions of this invention may contain a photoinitiator. Unless the composition is formulated specifically for use with electron beam curing, the energy curable composition will typically contain an addition polymerization photoinitiator that generates free radicals upon exposure to actinic radiation, such as ultraviolet light. Such a photoinitiator has one or more compounds that directly furnish free radicals when activated by actinic radiation. The photoinitiator may also contain a sensitizer that extends the spectral response into the near ultraviolet, visible or near infrared spectral regions. In free radical initiated curing systems, typically irradiation of a photoinitiator produces free radicals that initiate polymerization and/or crosslinking. Typically, only small amounts of photoinitiator are required to effectively initiate a polymerization, e.g. from about 0.5 wt.% to about 5 wt. % based on the total weight of the polymerizable (curable) solution. Typically, the photoinitiator is readily soluble in at least one of the major components of the energy curable solution; and it is preferably at least partially soluble in water. Still more preferably, the free radical curing system comprises a photoinitiator that is substantially soluble in one or more of the major components in the homogenous solution of the present invention. A wide variety of photoinitiators may be used in the aqueous compositions of this invention. Useful photoinitiators of this type are, for example, described in a review by B.M. Monroe and G.C. Weed entitled *"Photoinitiators for Free-Radical-Initiated Photoimaging Systems"*, Chem. Rev. **1993**, 93, 435-448, which is incorporated herein by reference. Preferred photoinitiators, suitable for use alone or in combination with other photoinitiators, are Irgacure 1173, Irgacure 500, Irgacure 184, Irgacure 2959 (Irgacure is a trademark and commercially available product of Ciba Specialty Additives, Tarrytown, NY), Esacure KIP 150, Esacure KIP EM and Esacure KIP DP 250 (Esacure is a Trademark and commercially available product of Lamberti, Gallarate, Italy).

Energy Curable Inks Prepared from Aqueous Solutions

As used herein, the term "ink" or "printing ink" has its conventional meaning, i.e., a colored liquid composed of a metallic pigment colorant, dispersed in a liquid vehicle. In particular, the energy curable ink of the present invention comprises: a metallic pigment and the energy curable, aqueous homogeneous compositions of this invention

5 fully described above. As discussed above, the oligomer contained in the vehicle can either be a partially water soluble oligomer, a water soluble oligomer, or combination thereof. A further alternative energy curable liquid vehicle, comprises an energy curable, aqueous solution of water and a water soluble, ethylenically unsaturated resin salt having neutralized acidic and basic functional groups, as discussed above.

10

Colorants

The energy curable inks of this invention contain one or more colorants such as metallic pigments or dyes dispersed therein. Metallic pigment colorants suitable for use
15 in the present invention include conventional metallic pigment colorants and metallic pigment dispersions such as silver metallic pigment dispersions and gold metallic pigment dispersions (e.g. RV 5025 and RV5049, commercially available from Eckart America L.P., Painesville, OH, USA). Pigment compositions which are a blend of conventional metallic pigment colorant and poly(alkylene oxide) grafted pigments are
20 also suitable for use in the invention.

Adjuvants

The energy curable printing inks of this invention may contain the usual
25 adjuvants to adjust flow, surface tension and gloss of the cured printing ink. Such adjuvants contained in inks typically are a surface-active agent, a wax, or a combination thereof. These adjuvants may function as leveling agents, wetting agents, dispersants, defrothers or deaerators. Additional adjuvants may be added to provide a specific function such as surface slip. Preferred adjuvants include fluorocarbon surfactants such
30 as FC-4430 (commercially available product of the 3M Company, St Paul, MN); silicones such as DC57 (commercially available product of Dow Chemical Corporation, Midland, MI), Byk 024, Byk 019, Byk 023, Byk 373, Byk 381, Byk 3500, Byk 3510, Byk 3530, Byk 361, Byk 363 (commercially available products of Byk Chemie, Wesel, Germany) Foamex N, Foamex 8030, Foamex 810, Airex 900, Tegorad 2100, Tegorad
35 2200N, Tegorad 2250N, Tegorad 2500, Tegorad 2600 (Foamex, Airex and Tegorad are trademarks and are commercially available products of Tego Chemie, Essen, Germany.), Addid 700, Addid 810, Addid 840, Addid 300, Addid 310, Addid 320 (Addid is a trademark and commercially available from Wacker Silicones Corp., Adrian, MI.); organic polymer surfactants like, Solspers 24000, Solspers 32000, Solspers 41090,

5 Solspers 20000, Solspers 27000 (Solspers is a trademark and commercially available from United Color Technology, Inc., Newton, PA.) Disperbyk 168, Disperbyk 184, Disperbyk 190, Disperbyk 192 (Disperbyk is a trademark and commercially available from Byk Chemie, Wesel, Germany.), Wet 500, Wet 505, Airex 920, Airex 910, Dispers 610, Dispers 605, Dispers 740, Dispers 750 and Dispers 760 (Dispers, Wet and Airex are trademarks and are commercially available from Tego Chemie, Essen, Germany.)
10 Surfanol 105E, Surfanol 420, Dynol 604 (Surfanol and Dynol are trademarks and are commercially available from Air Products and Chemicals Inc., Allentown, PA.); polyethylene wax; polyamide wax; polytetrafluoroethylene wax; and the like.

15 **Preparation of Energy Cured Metallic Ink Film**

An embodiment of this invention is a method of forming a film and/or a printed metallic ink image. Thus, the energy curable compositions of this invention may be applied to a variety of substrates and cured by a variety of methods for applications that
20 include protective, decorative and insulating coatings; potting compounds; sealants; adhesives; photoresists; textile coatings; and laminates on a variety of substrates, e.g., metal, rubber, plastic, wood, molded parts, films, paper, glass cloth, concrete, and ceramic. The energy curable compositions of this invention are particularly useful in the manufacture of coatings and printing inks for use in a variety of Graphic Art applications
25 and printing processes. Advantageously, the compositions of this invention cure without the prior removal of water. Moreover, the energy curable compositions derived therefrom, are particularly useful in the wet-trap printing applications as disclosed in co-pending Patent Application USSN 10/079,781.

The embodiment of this invention directed to a method for forming a cured,
30 water-resistant metallic ink on a substrate comprises applying to a substrate the energy curable, aqueous compositions of the invention to form a layer and subsequently subjecting the substrate to a source of actinic radiation. However, if the method is specifically directed to forming a water-resistant metallic inks, containing metallic colorants. The energy curable, aqueous composition may be any of the energy curable, aqueous compositions of this invention. Thus, the composition may comprise a
35 homogeneous solution of water; an ethylenically unsaturated oligomer; and an ethylenically unsaturated resin containing neutralized acidic or basic functional groups. The oligomer employed may be a partially or a completely water soluble oligomer or may be a combination of partially water soluble, completely water soluble and water

5 insoluble oligomers. Alternatively, the composition may comprise a homogeneous solution of water and an ethylenically unsaturated resin containing neutralized acidic or basic functional groups. As previously described the energy curable, aqueous composition may additionally require adding a photoinitiator, an adjuvant or a combination thereof.

10 The aqueous composition may be applied to the substrate surface without the colorant as a coating in a uniform layer using any conventional coating technique. Therefore, compositions of the present invention may be applied by spin coating, bar coating, roller coating, curtain coating or by brushing, spraying, etc. Alternatively, the aqueous composition may be applied image-wise to a substrate surface, for instance as
15 a printing ink, using any conventional industrial printing technique including flexographic, gravure, screen, lithographic, and ink jet printing.

The actinic radiation initiated cure is most effectively done with the water of the formula in place. Water as solvent lowers the viscosity permitting the reactive sites of polymerization to diffuse in the system and to propagate effectively to generate longer
20 chains. The viscosity point at which effective reaction ceases is known as the vitrification point. In the presence of water above a critical level, a very low residual functionality remains after initiation of the polymerization, as vitrification is delayed by the decreased viscosity. Water also decreases the level of dissolved oxygen in the coating. This fact leads to more rapid cure as well.

25 From the moment the metallic ink of the present invention is applied, water starts evaporating. UV lamps and electron beams under nitrogen flow provide heat and gas flow that accelerates water removal. Depending on the characteristics of the particular cure unit operating as a dryer, there is a maximum level of water that will be removed per unit time in the curing zone. Without implying a limit, it is evident from the
30 discussion above that a certain fraction of water must remain in the coating at the point of exit from the cure unit. In most cases, however, less water than the measured maximum can be coated without increasing the residual acrylic unsaturation, i.e., the rate of drying slows as the critical limit is approached. In our experience, the practical lower limit is 1/3 of the amount estimated from the maximum drying capacity.
35 Characteristic of having water in place at the point of cure, the compositions of the present invention at greater than 25 wt. % water in the liquid phase cure to such complete conversion that no acrylate unsaturation can be detected by the usual reflection infrared techniques used in the industry.

5

Substrate

The substrate and its surface may be composed of any typical substrate material such as plastics, metals, composites, papers, etc.; and the energy cured film or layer on the substrate may be used in a variety of applications. The substrate may be print stock typically used for publications or may be a packaging material in the form of a sheet, a container such as a bottle or can, or the like. In most instances, the packaging material is a polyolefin such as a polyethylene or a polypropylene, a polyester such as polyethylene terephthalate, or a metal such as an aluminum foil, a metalized polyester, or a metal container. Once the aqueous, homogeneous, energy curable metallic ink composition of the present invention is applied to the packaging material it may be used to contain any kind of liquid or solid material such as foods, drinks, cosmetics, biological materials or specimens, pharmaceuticals, etc.

The metallic printing ink compositions of this invention will now be illustrated by the following examples, however, the specification is not intended to be limited thereby.

Example 1

30

Letdown Varnish

To the aqueous resin salt described in co-pending U.S. Patent Application USSN _____ (58.0 g or 10%, resin concentrate containing 41.5 wt. % resin solids in water, amine-neutralized (Sun 924-1069, of Sun Chemical Corporation, Fort Lee, NJ) to pH 6.5) was added the partially water soluble, ethylenically unsaturated, oligomer (68.5%, Laromer 8765 Laromer is a trademark and commercially available product of BASF Corporation, Mount Olive, NJ and (10.5%, Sartomer SR610, which is a commercially available product of Sartomer Company, Exton PA, USA). A UV stabilizer (0.6%, Florstab UV-1, a commercially available product of Kromachem Limited, Watford, England), surfactant (2.0%, Silwet L-7604, a commercially available product of OSI), Silicone defoamer (0.1%, BYK 019, BYK Chemie GmbH, Wesel, Germany), ammonia (0.3% containing 30% NH₄OH) and water (8%) were then added and the resulting composition stirred with a Cowles blade mixer to give a homogeneous mixture.

5

Example 2

Silver Ink formulation

10 The letdown varnish formula described in Example 1 (60%) was added to a silver metallic pigment dispersion (40.0%, RV5025, commercially available from Eckart America L.P., Painsville, Ohio, USA) and mixed until a single phase was formed.

Example 3

15

Gold Ink Formulation

The letdown varnish formula as described in Example 1 (60%) was added to a gold metallic pigment dispersion (40.0%, RV5049, commercially available from Eckart America L.P., Painsville, Ohio, USA) and mixed until a single phase was formed.

20

Those skilled in the art having the benefit of the teachings of the present invention as hereinabove set forth, can effect numerous modifications thereto. These modifications are to be construed as being encompassed within the scope of the present invention as set forth in the appended claims.